

United States Patent [19]

Sapers et al.

[11] Patent Number: 4,814,192

[45] Date of Patent: Mar. 21, 1989

[54] **PROCESS FOR PRESERVING RAW FRUITS AND VEGETABLES USING ASCORBIC ACID ESTERS**

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[21] Appl. No.: 123,451

[22] Filed: Nov. 18, 1987

[51] Int. Cl.⁴ A23B 4/12; A23B 7/10; A23L 1/277

[52] U.S. Cl. 426/268; 426/321; 426/323; 426/326; 426/333

[58] Field of Search 426/321, 268, 323, 326, 426/330, 330.5, 330.6, 331, 333

[56] **References Cited**

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phoric Esters of L-Ascorbic Acid," Carbohydr. Res., 67: 127-138 (1978).

R. C. Cousins et al., "Synthesis of 6-Fatty Acid Esters of L-Ascorbic Acid," J. Am. Oil Chem. Soc., 54: 308-312 (1977).

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[57] ABSTRACT

A process of inhibiting enzymatic browning in mechanically injured, raw fruit and vegetable products, including juices, comprising treating the products with ascorbic acid-2-phosphate esters and ascorbyl-6-fatty acid esters, individually or in combination. The treatments may be applied in an aqueous carrier and may further comprise other browning inhibitors, polyphenol oxidase inhibitors, emulsifying agents, dispersing agents and complexing agents. Treatments tend to delay or prevent the onset of enzymatic browning or, once browning has begun, to limit the extent of enzymatic browning. Also disclosed are novel browning.

11 Claims, No Drawings

PROCESS FOR PRESERVING RAW FRUITS AND VEGETABLES USING ASCORBIC ACID ESTERS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to the preservation of raw fruits, vegetables and their juices. More particularly, the present invention relates to the use of certain ascorbic acid esters, and compositions thereof, to control enzymatic browning in raw fruit and vegetable products.

2. Description of the Prior Art

Browning of raw fruits and vegetables due to mechanical injury, e.g., peeling, cutting, slicing, crushing etc., during postharvest processing has caused major losses in quality and value in the affected commodities. This enzymatic browning results from the polyphenol oxidase-catalyzed oxidation of phenolic compounds to O-quinones which sequentially polymerize to form dark-colored pigments.

Heretofore, efforts to control enzymatic browning in unblanched, cut fruits and vegetables have primarily involved sulfite treatments to preserve their natural color. However, recent concerns over the adverse health effects from sulfites has stimulated much research to develop effective sulfite substitutes. A number of sulfite substitutes, mostly combinations of ascorbic or erythorbic acid with citric acid, phosphates and chlorides, have been developed. These formulations, however, do not usually provide the extended protection obtained with sulfites. This deficiency is due largely to the rapid oxidation of ascorbate or erythorbate, catalyzed by endogenous enzymes and copper in the raw commodity.

Consequently, there exists a need in the food industry for sulfite alternatives which are safe, economical and effective.

SUMMARY OF THE INVENTION

We have now developed a process of preserving mechanically injured raw fruit and vegetable products, including juices, by controlling enzymatic browning in these commodities. The invention process involves subjecting the fruit and vegetable products to certain ascorbic acid esters and/or compositions thereof, for a period of time sufficient to inhibit browning. The treatments offer suitable replacements for potentially toxic sulfite treatments currently being used to preserve these commodities.

Accordingly, it is an object of the present invention to provide a novel process for preserving raw fruits, vegetables and their juices.

Another object is to provide a process for preserving these fruits and vegetables products which eliminates the use of sulfites.

Further, it is an object of the invention to provide novel compositions useful to inhibit enzymatic browning in mechanically injured fruits and vegetables and their juices.

In general, we have accomplished the foregoing objects by providing a process for preserving mechanically injured raw fruits and vegetables comprising subjecting the fruits and vegetables to an effective antibrowning amount of an antibrowning compound selected from the group consisting of (a) ascorbic acid esters formed by reacting ascorbic acid at the number 2 carbon atom with a phosphoric acid; and (b) ascorbyl-

fatty acid esters formed by reacting ascorbic acid at the number 6 carbon atom with a fatty acid. The effect of treatments in accordance with the invention process is to lengthen the storage life of mechanically injured fruit and vegetable products by either extending the time before the onset of browning, i.e., lag time, or once browning has begun, decreasing the extent or rate of enzymatic browning.

DETAILED DESCRIPTION OF THE INVENTION

The ascorbic acid phosphate esters useful in the invention process are those esters in which the number 2 carbon atom of ascorbic acid has been esterified with a phosphoric acid. Examples of such esters include ascorbic acid-2-phosphate, ascorbic acid-2-diphosphate, ascorbic acid-2-triphosphate and ascorbic acid-2-polyphosphate. The esters of ascorbic acid may be prepared by reacting ascorbic acid with salts of a metaphosphoric acid in accordance with the procedure as described in Seib et al., U.S. Pat. No. 4,647,672, issued Mar. 3, 1987. Ascorbic acid-2-phosphate may also be prepared by the condensation of ascorbic acid and phosphoric acid using the procedure as described in Lee et al. [Carbohydrate Res. 67: 127-138 (1978)].

The ascorbyl-fatty acid esters useful in the invention process are those esters in which the number 6 carbon atom of ascorbic acid is reacted with a fatty acid. Suitable fatty acids include palmitic, lauric, decanoic, octanoic acids and the like. The ascorbyl-6-fatty acid esters may be prepared by reacting ascorbic acid with excess fatty acid in accordance with the procedure as described in R. C. Cousins et al. [J. Am. Oil Chem. Soc. 54: 308-312 (1977)].

For optimum results, the compounds useful in the invention process should be used in substantially pure form, that is, free of undesirable contaminants that tend to mask or otherwise inhibit their effectiveness. It is within the compass of the invention to use the ascorbic acid esters either individually or in combination. The compounds and/or compositions may also be used in combination with known browning inhibitors, such as ascorbic acid or erythorbic acid, or in combination with polyphenol oxidase inhibitors such as cinnamic acid, certain other phenolic acids, citric acid or the like. In addition, the compositions of the invention may include conventional additives such as emulsifiers, acidulants and dispersing agents.

Suitable emulsifiers for use in the invention compositions include, but are not limited to, monoglycerides, diglycerides, glycol esters of fatty acids, polyglycol esters of fatty acids and mixtures thereof. Preferably, the emulsifiers are selected to have a low to moderate hydrophilic/lipophilic balance. Suitable dispersing agents include xanthan gum, carboxymethylcellulose, guar gum, pectin and the like. The term "acidulants" as used herein is used to designate any food-grade additive which serves to lower the pH of the invention ester compositions to a value that is below the optimal pH value for polyphenol oxidase. Suitable acidulants include citric acid, gluconic acid, lactic acid and the like.

The compositions of the invention may also include complexing agents such as citric acid, cyclodextrins and the like. A particular effective complexing agent found to enhance antibrowning activity of the ascorbic acid and its ester derivatives is an acidic polyphosphate having a 1:1 ratio of $P_2O_5:Na_2O$. When used, the acidic

polyphosphate, as well as the other additives mentioned hereinabove, should be used in concentrations which, as readily determined by one skilled in the arts, will not interfere with the effectiveness of antibrowning agents of the invention.

In use, the ester compositions are dispersed directly in an aqueous carrier. Because of the insolubility of ascorbyl-fatty acid esters in water, it may be necessary to first dissolve the fatty acid esters in a more soluble medium, e.g., ethyl alcohol or propylene glycol, prior to addition to an aqueous system. For example, a stable aqueous dispersion of ascorbyl palmitate was prepared by dissolving the ester with a low hydrophilic/lipophilic balanced emulsifying agent in ethyl alcohol. The emulsifier-ascorbyl palmitate solution was then added to an aqueous solution containing a phosphate buffer, pH 7, heated at about 75° C. Thereafter, the aqueous dispersion was cooled to about 40° C.-50° C. for immediate use.

Aqueous solutions or dispersions of the ester compositions may be applied to sliced fruits and vegetables by conventional methods such as dipping or spraying. Exemplary concentrations useful for dipping or spraying range from about 22.27 mM to 181.8 mM. Because of the insolubility of the ascorbyl-fatty acid esters, lower concentrations of the esters may be used, for example, from about 2.4 mM to 22.1 mM. Aqueous solutions or dispersions of the ester compositions of the invention are added directly to juice systems in relative lower concentrations than used for sprays or dips. For example, concentrations may range from about 0.28 mM to about 4.4 mM.

The process of the invention is useful to preserve the storage life of any mechanically damaged fruit or vegetable which undergoes enzymatic browning, i.e., polyphenol oxidase oxidation of polyphenols. Consequently, the invention procedure is useful to preserve the products of a variety of raw fruits and vegetables including, but not limited to, apples, pears, bananas, avocados, potatoes, lettuce, mushrooms and the like.

The process of the invention is further demonstrated by the following examples which are intended only to further illustrate the invention and not to limit the scope of the invention as defined by the claims.

EXAMPLE 1

The effectiveness of the process of the invention was evaluated in a raw apple juice system and on standardized cut apple surfaces.

Apple samples representing common cultivars were obtained from local food stores during the fall and winter of 1986-87 and stored briefly at 4° C. until used. One hour prior to use, fruits were removed from refrigeration and equilibrated at room temperature (ca 20° C.).

Browning at Cut Surfaces

Each apple was cut in half along the stem axis, and the halves were positioned in a Petri dish, cut side down, under an electric cork borer (Sargent-Welch, Skokie, IL) so that uniform plugs could be bored perpendicular to the cut surface, on either side of the point of greatest thickness, with a 22 mm stainless steel cutting tube. At the start of an experiment, a transverse cut was made in the plug, at its midpoint, yielding two half-plugs sharing a common cut surface. An arrow was cut at the opposite end of each plug half to mark its orientation during reflectance measurements.

Apple plugs were treated by dipping in freshly prepared aqueous solutions or dispersions of the targeted browning inhibitor for 90 seconds. Treatments were applied to one plug half from each pair of plug halves.

The remaining plug halves which were to be used as untreated controls were dipped in pure water. After dipping, the plug halves were drained, blotted dry and held for 7 hrs at 20° C.

Color changes were measured in treated samples and untreated controls during storage at 20° C. Colorimetry was performed with a Gardner XL-23 Tristimulus Colorimeter (Pacific Scientific, Silver Spring, MD), operated with large diameter illumination and with a 19 mm opening aperture plate. The instrument was standardized against a white tile ($Y=84.60$, $X=82.21$, $Z=97.64$) before each measurement. The transversely cut surface of a plug was centered over the aperture, oriented so that the arrow cut in the opposite end pointed away from the colorimeter operator. Values of the tristimulus coordinates in the L, a, b and Y, X, Z systems were recorded at 1, 10, 30, 60, 90, 120, 150, 180, 240, 300, 360 and 420 minutes. Between measurements, plugs were held in covered glass crystallizing dishes to minimize dehydration at the cut surface. The tristimulus coordinates were plotted against log time, and the slopes of linear portions of these curves were obtained by linear regression. Lag times were obtained from these graphs by direct measurement.

Browning in Juice

Juice samples were prepared from individual Granny Smith apples with an Acme Supreme Model 6001 Juicer. The freshly prepared juices from 2 or 3 apples were combined, briefly stirred to ensure uniformity and then rapidly dispersed by burette into cylindrical clear glass optical cells containing the targeted antibrowning composition.

Colorimetry of the juice samples were performed as described above but with the optical cell placed in a 50 mm diameter support ring in place of the 19 mm aperture plate. Tristimulus values were recorded at frequent intervals up to 24 hours and were plotted against time rather than log time. Lag times were obtained from these graphs by direct measurement.

Alternatively, browning in apple juice was determined spectrophotometrically by taking, at 15 minute interval, 10 ml aliquots of a 100-125 ml juice sample which was continually mixed slowly by stirring. Thereafter, the aliquots were clarified by a modification of the method of Meydavi et al. [J. Agric. Food Chem. 25: 602 (1977)] which entails rapid mixing with an equal volume of 95% ethanol and 0.3 g Celite Analytical Filter Aid (Fisher Scientific, Pittsburgh, PA) followed by filtration through Whatman No. 50 paper under suction. The absorbance of the filtrates was determined at 420 nm with a Perkin-Elmer Model 552 UV-visible spectrophotometer (Perkin-Elmer, Oak Brook, IL).

Various antibrowning compositions of the invention were tested for browning inhibition using the process of the invention. The effectiveness of treatments was expressed in terms of percent inhibition. For purposes of the invention, percent inhibition is defined as the change in the reflectance or absorbance of the treated sample over a specified time interval (ΔL treatment) subtracted from the change in reflectance or absorbance in the corresponding untreated control (ΔL control), expressed as a percentage of the change in the control:

Dips containing combinations of Sporix with ascorbic acid or ascorbic acid-2-phosphate were also highly effective in inhibiting enzymatic browning on the cut surfaces of apple plugs. As shown in Table IV, apple plugs dipped in 56.8 mM (1%) ascorbic acid in combination with 0.25% Sporix showed little or no evidence of browning after 24 hr at 20° C. while untreated controls discolored within several hours (Expt. D). Sporix alone was ineffective under these conditions.

¹In 0.05 M phosphate buffer, pH 7.

Expt.	Treatment	Percent Inhibition ^b						L ^c Control
		L-value			a-value			
		1 hr	6 hr	24 hr	1 hr	6 hr	24 hr	
8	0.29% Sporix	73	74	73	56	59	50	-5.7

TABLE III-continued

Inhibition of enzymatic browning in Granny Smith juice by Sporix and combinations of Sporix with ascorbic acid (AA)								
Expt.	Treatment	Percent Inhibition ^b						L ^c
		L-value			a-value			
		1 hr	6 hr	24 hr	1 hr	6 hr	24 hr	
9	0.59% Sporix	107	119	128	82	82	73	-5.7
	0.88% Sporix	101	119	127	83	80	74	-5.7
	0.57% mM AA	68	-22	-28	68	-4	-8	-5.7
	0.14% Sporix + 0.57 mM AA	107	26	10	66	41	34	-3.2
	0.29% Sporix + 0.57 mM AA	115	110	132	72	70	56	-3.2
	0.14% Sporix	14	15	15	14	34	28	-3.2
	0.29% Sporix	59	59	58	34	48	43	-3.2
10	0.57 mM AA	76	-34	-32	44	-16	-17	-3.2
	0.29% Sporix + 0.57 mM AA	57	80	—	83	73	—	-6.6
	0.29% Sporix + 1.14 mM AA	89	102	—	71	68	—	-6.6
	0.29% Sporix	66	91	—	5	47	—	-6.6
	0.57 mM AA	9	-28	—	-12	-30	—	-6.6
	1.14 mM AA	115	-12	—	76	-30	—	-6.6
	0.29% Sporix + 0.57 mM AA	102	110	112	78	84	76	-6.1
11	(pH 3.1)							
	0.29% Sporix + 0.57 mM AA ^d	68	33	25	64	58	52	-6.1
	(pH 3.3)							
	0.57 mM AA (pH 3.3)	43	6	26	37	5	-5	-6.1

^bBased on difference in L- or a- value between specified time and 5 min.
^cDifference in L-value between 60 min and 5 min.
^dAdjusted to pH of control with 10% NaOH.

TABLE IV

Inhibition of enzymatic browning of cut surface of apple by combinations of Sporix and ascorbic acid (AA) or ascorbic acid-2-phosphate (AAP)										
Expt.	Cultivar	Dip solution	Percent Inhibition				Lag (min) ^b		Browning rate (min ⁻¹)	
			L-value		a-value		L	a	L	a
			6 hr	24 hr	6 hr	24 hr				
A	Red Delicious	22.7 mM AA + 0.25% Sporix	124	123	78	57	>360	180	0	0.6
		22.7 mM AA + 0.50% Sporix	104	139	80	49	>360	180	0	0.5
		22.7 mM AA	71	83	56	41	45	60	-2.7	1.4
		0.25% Sporix	41	51	32	30	10	0	-1.4	0.4
		0.50% Sporix	28	43	-5	-9	17	10	-1.2	0.4
B	Winesap	22.7 mM AA + 0.25% Sporix	69	58	64	44	40	60	-2.0	1.6
		22.7 mM AA + 0.50% Sporix	97	81	93	68	>360	>360	0	0
		22.7 mM AA	-5	28	12	10	20	17	-5.6	2.6
		0.25% Sporix	43	43	44	38	10	10	-2.5	1.5
		0.50% Sporix	52	30	44	30	10	0	-1.3	0.6
C	Winesap	22.7 mM AA + 0.25% Sporix	107	111	92	78	>360	120	0	0.4
		22.7 mM AAP + 0.25% Sporix	107	116	78	63	>360	10	0	0.6
		22.7 mM AA	58	71	46	44	22	25	-4.5	2.4
		22.7 mM AAP	90	112	63	57	30	0	-1.6	0.4
		0.25% Sporix	51	-34	34	-41	10	10	-2.1	1.4
D	Red Delicious ^c Winesap ^d	56.8 mM AA + 0.25% Sporix	109 ± 18	111 ± 32	98 ± 3	84 ± 12	>360	>360	0	0
		56.8 mM AA + 0.25% Sporix	109 ± 25	109 ± 25	99 ± 4	91 ± 9	>360	>360	0	0

^bSlope of L or "a" vs log time curve.
^cMean percent inhibition and standard deviation for 7 duplicate trials.
^dMean percent inhibition and standard deviation for 5 duplicate trials.

We claim:

1. A process for preserving mechanically injured raw fruit and vegetable products against enzymatic browning comprising subjecting said fruit and vegetable products to an effective antibrowning amount of a browning inhibitor selected from the group consisting of (A) an ascorbic acid ester from the group consisting of ascorbic acid-2-phosphate, ascorbic acid-2-diphosphate, ascorbic acid-2-triphosphate and ascorbic acid-2-polyphosphate; (B) an ascorbic acid ester selected from the group consisting of ascorbyl-6-palmitate, ascorbyl-6-laurate, ascorbyl-6-decanoate and ascorbyl-6-octanoate; and (C) combinations thereof, for a period of time sufficient to inhibit browning.
2. The process of claim 1 wherein the browning inhibitor is an ascorbic acid ester selected from the group consisting of ascorbic acid-2-phosphate, ascorbic acid-2-diphosphate, ascorbic acid-2-triphosphate and ascorbic acid-2-polyphosphate.
3. The process of claim 1 wherein the browning inhibitor is an ascorbic acid ester selected from the group

- consisting of ascorbyl-6-palmitate, ascorbyl-6-laurate, ascorbyl-6-decanoate and ascorbyl-6-octanoate.
4. The process of claim 1 wherein the browning inhibitor is contained in an aqueous carrier solution.
5. The process of claim 1 wherein the browning inhibitor further comprises ascorbic acid.
6. The process of claim 1 wherein the browning inhibitor further comprises erythorbic acid.
7. The process of claim 1 wherein the browning inhibitor further comprises a polyphenol oxidase inhibitor.
8. The process of claim 1 wherein the browning inhibitor further comprises an emulsifying agent.
9. The process of claim 1 wherein the browning inhibitor further comprises a complexing agent.
10. The process of claim 9 wherein the complexing agent is an acidic polyphosphate having a 1:1 ratio of P₂O₅:Na₂O.
11. The process of claim 1 wherein the raw fruit and vegetable product is a juice.

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